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(54) METHOD FOR PRODUCING 3,3'-DIALLYL-4,4'- DIHYDROXYDIPHENYLSULFONE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone, by which the 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone useful as a developing agent for heat-sensitive recording materials and scarcely containing components causing halation on the surfaces of substrates can be obtained in a high yield.

SOLUTION: This method for producing 3,3'-diallyl-4,4'-dihydroxydiphenyl sulfone by subjecting 4,4'-diallyloxydiphenylsulfone to a thermal rearrangement reaction, is characterized by subjecting the 4,4'-diallyloxydiphenylsulfone to the thermal rearrangement reaction in the presence of an amine compound in an amount of 0.01 to 1 wt.% and/or an antioxidant in an amount of 0.01 to 1 wt.% based on the 4,4'-diallyloxydiphenylsulfone, while controlling the total amount of alkalis contained in the 4,4'-diallyloxydiphenylsulfone to ≤ 50 ppm (weight ratio) converted into sodium hydroxide.

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CLAIMS

[Claim(s)]

[Claim 1]In a method of carrying out the heating rearrangement reaction of the 4,4'-diaryl oxydi phenylsulfone, and manufacturing 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, An alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone, It converts into sodium hydroxide and costs below 50 ppm (weight ratio), A manufacturing method of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone carrying out a heating rearrangement reaction to a 4,4'-diaryl oxydi phenylsulfone under 0.01 to 1% of the weight of existence of an amine compound and/or 0.01 to 1% of the weight of an antioxidant.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone. Still more detailed 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone with this invention useful as a color developer of a thermal recording material, There are few ground fogging ingredients and they are related with the manufacturing method of the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone which can be obtained with high yield.

[0002]

[Description of the Prior Art]3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone is a substance useful as a color developer of a thermal recording material.

Various manufacturing methods are tried.

For example, to JP,61-89090,A and JP,62-53957,A. As a manufacturing method of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone with little fogging, 3-allyl-4-hydroxy-4'-allyloxy diphenylsulfone is made into 5 to 20% of the weight of a 4,4'-diaryl oxydi phenylsulfone, The method of controlling the yield of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone to 90 or less % of the weight, and terminating a heating transition reaction is proposed. After extracting and ****(ing) a reaction mixture with lye, recrystallization refined using the partially aromatic solvent of a dichloro alkane system solvent, an aromatic solvent, an alcohol system, or a glycol system solvent, and 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone has been obtained. In the powder X-ray diffractometry JP,11-29549,A has little ground fogging at the time of wet heat at high sensitivity, and DSC (Te) is not less than 149 ** as a thermal recording material excellent in image keeping quality, and according to Cu-K alpha rays, Even if small, it is a crystal form characterized with the X diffraction figure which reaches and has a peak in 22.0 angle-of-diffraction (2 theta) [**] 7.2, and the thermal recording material in which the content of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone contains 96% of the weight or more of a crystal is

proposed. The heating rearrangement of the 4,4'-diaryl oxydi phenylsulfone is carried out in the inactive nonaqueous solubility organic solvent of a high boiling point, Carry out the generated amount of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone to 89 to 93% of the weight, and a reaction is ended, . [whether after extracting with an alkaline aqueous solution, acid uses and refines activated carbon in the liquid which carried out partial neutralization, subsequently to the inside of an acid aqueous solution it leads, and a crystal is deposited, and] Or water and a nonaqueous solubility organic solvent were added after extraction by the alkaline aqueous solution, the water layer and the oil reservoir were separated, and 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone has been obtained by adding an acid aqueous solution to a water layer. In the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone used as a color developer of a thermal recording material, The 5-(3-allyl-4-hydroxy) phenyl slufonyl 1-oxa 2-methylindan generated by a heating rearrangement reaction, Ground fogging will become intense if many by-products, such as 3-allyl-4-hydroxy-4'-allyloxy diphenylsulfone and 3-allyl-4,4'-dihydroxy diphenylsulfone, are contained. In the above-mentioned manufacturing method, since there are many ground fogging ingredients which carry out a byproduction at the time of a rearrangement reaction, even if the removing becomes insufficient, and ground fogging occurs or it can fully perform removal of a ground fogging ingredient, yield becomes low and methods of it being cheap and manufacturing industrially include a difficulty. For this reason, the method of manufacturing economically 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone with few ground fogging ingredients with high purity was called for.

[0003]

[Problem(s) to be Solved by the Invention]This invention 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone useful as a color developer of a thermal recording material, There are few ground fogging ingredients and they are made for the purpose of providing the manufacturing method of the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone which can be obtained with high yield.

[0004]

[Means for Solving the Problem]As a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved, this invention persons an alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone, By converting into sodium hydroxide, costing below 50 ppm (weight ratio), and carrying out a heating transition reaction under existence of a little amine compounds and/or an antioxidant, It finds out that it becomes possible to obtain 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone of a high grade with high yield, and came to complete this invention based on this knowledge. Namely, in a method of this invention carrying out the heating rearrangement reaction of the 4,4'-diaryl oxydi phenylsulfone, and manufacturing 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, An alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone, It converts into sodium hydroxide and

costs below 50 ppm (weight ratio), As opposed to a 4,4'-diaryl oxydi phenylsulfone. A manufacturing method of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone carrying out a heating rearrangement reaction under 0.01 to 1% of the weight of existence of an amine compound and/or 0.01 to 1% of the weight of an antioxidant is provided.

[0005]

[Embodiment of the Invention]In the manufacturing method of the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone of this invention, In the method of carrying out the heating rearrangement reaction of the 4,4'-diaryl oxydi phenylsulfone, and manufacturing 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, The alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone, It converts into sodium hydroxide, below 50 ppm (weight ratio) are cost, and a heating rearrangement reaction is carried out to a 4,4'-diaryl oxydi phenylsulfone under 0.01 to 1% of the weight of existence of an amine compound and/or 0.01 to 1% of the weight of an antioxidant. In this invention method, the 4,4'-diaryl oxydi phenylsulfone used as the raw material of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, It is manufactured by carrying out the dehydrohalogenation reaction of 4,4'-dihydroxy diphenylsulfone and the allyl halide into an organic solvent under existence of alkali, such as hydroxide of an alkaline metal, hydroxide of alkaline-earth metals, and carbonate. Therefore, in a 4,4'-diaryl oxydi phenylsulfone. Hydroxide of an alkaline metal, hydroxide of alkaline-earth metals, carbonate, a halogenide, The alkali metal salt of 4,4'-dihydroxy diphenylsulfone, the alkaline earth metal salt of 4,4'-dihydroxy diphenylsulfone, Mixing of impurities, such as alkali metal salt of 4-allyloxy 4'-hydroxy diphenylsulfone and alkaline earth metal salt of 4-allyloxy 4'-hydroxy diphenylsulfone, is not avoided. The total amount can be quantified by using all of these impurities as an alkali component.

[0006]In this invention method, the alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone is converted into sodium hydroxide, and a heating rearrangement reaction is carried out as below 50 ppm (weight ratio). The alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone, After dissolving a 4,4'-diaryl oxydi phenylsulfone in organic solvents, such as dimethyl sulfoxide, and adding sodium hydroxide solution, it can ask by titrating using chloride, comparing that it is blank, and converting a content alkali total amount into sodium hydroxide. The alkali total amount contained in the 4,4'-diaryl oxydi phenylsulfone used as a raw material, There is no restriction in particular in the method of converting into sodium hydroxide and carrying out below 50 ppm (weight ratio), For example, among an organic solvent, the crystal which might be made to react is filtered, 4,4'-dihydroxy diphenylsulfone and an allyl chloride are washed under existence of alkali, and a humidity 4,4'-diaryl oxydi phenylsulfone crystal thing is obtained. Next, by putting a humidity 4,4'-diaryl oxydi phenylsulfone crystal thing and warm water into a reaction vessel or a mixed iron pot, and filtering, washing and drying after agitation mixing at 40-80 **, A content alkali total amount can

obtain the 4,4'-diaryl oxydi phenylsulfone which is below 50 ppm (weight ratio).

[0007]If the content alkali total amount converted into sodium hydroxide carries out the heating rearrangement reaction of the 4,4'-diaryl oxydi phenylsulfone over 50 ppm (weight ratio), Hydroxide of an alkaline metal, hydroxide of alkaline-earth metals, carbonate, a halogenide, The alkali metal salt of 4,4'-dihydroxy diphenylsulfone, the alkaline earth metal salt of 4,4'-dihydroxy diphenylsulfone, The alkali metal salt of 4-allyloxy 4'-hydroxy diphenylsulfone, The alkaline earth metal salt of 4-allyloxy 4'-hydroxy diphenylsulfone, etc. configure in the phenolic hydroxyl group generated by oxygen and the rearrangement reaction of the ether bond, or by a complex, formation of a salt, etc. The detailed mechanism is unknown although it is thought that a side reaction is promoted and by-products including a ground fogging ingredient generate. The 5-(3-allyl-4-hydroxy) phenyl sulfonyl 1-oxa 2-methylindan which is a ground fogging ingredient when the alkali total amount to contain exceeds 50 ppm (weight ratio), 3-allyl-4-hydroxy-4'-allyloxy diphenylsulfone, Generation of 3-allyl-4,4'-dihydroxy diphenylsulfone etc. is promoted, and the subgeneration reaction from 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone occurs, Refining becomes difficult and causes a yield drop for the purity fall of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, generating of a ground fogging ingredient, and ground fogging ingredient removal.

[0008]As hydroxide of the alkaline metal contained in a 4,4'-diaryl oxydi phenylsulfone, There are sodium hydroxide, a potassium hydrate, etc. and as hydroxide of alkaline-earth metals, There are magnesium hydroxide, calcium hydroxide, etc. and as carbonate, There are sodium carbonate, potassium carbonate, magnesium carbonate, calcium carbonate, sodium bicarbonate, potassium bicarbonate, etc., and as a halogenide, There are sodium chloride, potassium chloride, a calcium chloride, a magnesium chloride, a sodium bromide, potassium bromide, a calcium bromide, a magnesium bromide, etc. There is no restriction in particular in the amine compound used for this invention method, for example, N,N-dimethylaniline, N,N-diethylaniline, dimethylamino pyridine, benzotriazol, diethylenetriamine, dimethylbenzylamine, etc. can be mentioned. A by-product generates with advance of the heating rearrangement reaction of a 4,4'-diaryl oxydi phenylsulfone. In order that an amine compound may promote advance of a main reaction by reacting under existence of an amine compound, it is thought that generating of a by-product is controlled. There is a possibility that the effect which controls a by-product as the amount of the amine compound used is less than 0.01 % of the weight to a 4,4'-diaryl oxydi phenylsulfone may not fully be demonstrated. If the amount of the amine compound used exceeds 1 % of the weight to a 4,4'-diaryl oxydi phenylsulfone, will configure in the phenolic hydroxyl group which the superfluous amine compound generated by the rearrangement reaction, or by formation of a complex or a salt. Conversely, there is a possibility that a side reaction may be promoted and a ground fogging ingredient (Indang object) may increase.

[0009] There is no restriction in particular in the antioxidant used for this invention method, and For example, hydroquinone monomethyl ether, Hydroquinone monoethyl ether, 3,5-di-t-butyl-4-hydroxytoluene, 2,2'-methylenebis (6-t-butyl-3-methyl phenol), Phenolic antioxidants, such as 1,1,3-tris(2-methyl-4-hydroxy-5-t-buthylphenyl) butane, 3,3'-didodecyl thiodipropionate, 3,3'-ditetradecyl thiodipropionate, The Lynn system antioxidants, such as sulfur-systems antioxidants, such as 3,3'-dioctadecyl thiodipropionate, phosphorous acid triphenyl, diphenyl phosphite isodecyl, and phosphorous acid tris (nonylphenyl), etc. can be mentioned. The coloring accompanying advance of a reaction can be controlled by performing the heating rearrangement reaction of a 4,4'-diaryl oxydi phenylsulfone under existence of an antioxidant. There is a possibility that the effect which controls coloring as the amount of the antioxidant used is less than 0.01 % of the weight to a 4,4'-diaryl oxydi phenylsulfone may not fully be demonstrated. When the amount of the antioxidant used exceeds 1 % of the weight to a 4,4'-diaryl oxydi phenylsulfone, there is a possibility that the by-product of a reaction may increase. In this invention method, the heating rearrangement reaction of a 4,4'-diaryl oxydi phenylsulfone can be performed by heating at 190-220 ** in inactive nonaqueous solubility organic solvents, such as a non-solvent or an aliphatic hydrocarbon solvent which has a high boiling point, and an aromatic organic solvent. Operation of the alkaline extraction of a reaction mixture, solvent extraction, washing, ****, recrystallization, etc. can refine after ending reaction, and the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone which has the performance outstanding as a color developer of a thermal recording material can be obtained.

[0010]

[Example] Although an example is given to below and this invention is explained to it still in detail, this invention is not limited at all by these examples. In the example and the comparative example, the content alkali total amount was calculated as follows. Namely, 30 g of 4,4'-diaryl oxydi phenylsulfones are dissolved in the dimethyl sulfoxide 450g, After adding 1/50 mol / L sodium hydroxide solution 10mL, the content alkali total amount was converted into a part for sodium hydroxide as compared with the value when it titrated using 1/100 mol / L chloride, and it titrates without adding a 4,4'-diaryl oxydi phenylsulfone.

In an example 1 4 Thu mouth flask, the content alkali total amount converted into sodium hydroxide 413 g of 5 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfones, Diana FURESHIA W-8 [Idemitsu Kosan, Inc.] 275 g, kerosene [large ***** , Inc.] 275g, 0.4g of N.N-dimethylaniline, and the hydroquinone monomethyl ether 0.4g were prepared, and the heating rearrangement reaction was carried out at 205-210 ** under the nitrogen air current for 7 hours. The HPLC composition ratio (area percentage) of the reaction mixture after a reaction, 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone. (It abbreviates to a JI rearrangement object hereafter.) A 92.3% and 5-(3-allyl-4-hydroxy) phenyl slufonyl 1-oxa 2-methylindan. (It abbreviates to the Indang object hereafter.) It was 3-allyl-4,4'-dihydroxy diphenylsulfone (it abbreviates to monoallyl

object hereafter.) 0.8% 1.7% 3-allyl-4-hydroxy-4'-allyloxy diphenylsulfone (it abbreviates to mono- rearrangement object hereafter.) 1.8%. This reaction mixture was cooled, the sodium hydroxide solution 715g was added 13% of the weight, after carrying out a settlement slice, lower layer alkaline aqueous solution and activated carbon 39g were taught to the 4 Thu mouth flask, decoloring treatment was carried out at 80 ** for 1 hour, and the ** exception carried out activated carbon. Decoloring treatment liquid was taught to the 4 Thu mouth flask, and the ** exception carried out the crystal which trickled the sulfuric acid 184g 50% of the weight, and ****(ed) and deposited at 60 **. The crystal which the ** exception used as the 4 Thu mouth flask, and 780 g of ethanedichloride were taught, and after adding 9.4 g of isopropanol and carrying out heating flowing back, it cooled to 25 **. The ** exception carried out the precipitated crystal and it washed using 300 g of ethanedichloride, and it dried and the 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 306g was obtained. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 97.1% of a JI rearrangement object, and 0.2% of the Indang object. Except that the content alkali total amount used a 15 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone instead of the content alkali total amount used in example 2 Example 1 being a 5 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone, it reacted like Example 1. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 92.0% of a JI rearrangement object, 1.9% of the Indang object, 1.9% of a mono- rearrangement object, and 0.7% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 301g was obtained by processing like Example 1. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 97.1% of a JI rearrangement object, and 0.3% of the Indang object. Except that the content alkali total amount used a 30 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone instead of the content alkali total amount used in example 3 Example 1 being a 5 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone, it reacted like Example 1. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.3% of a JI rearrangement object, 2.3% of the Indang object, 1.6% of a mono- rearrangement object, and 0.7% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 289g was obtained by processing like Example 1. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.5% of a JI rearrangement object, and 0.3% of the Indang object. Except that the content alkali total amount used a 45 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone instead of the content alkali total amount used in example 4 Example 1 being a 5 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone, it reacted like Example 1. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 90.9% of a JI rearrangement object, 2.9% of the Indang object, 1.5% of a mono- rearrangement object, and

0.6% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 285g was obtained by processing like Example 1. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.3% of a JI rearrangement object, and 0.4% of the Indang object.

[0011] Instead of 0.4 g of N.N-dimethylaniline used in example 5 Example 2, it reacted like Example 2 except having used 0.08 g of N.N-dimethylaniline. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 90.5% of a JI rearrangement object, 2.0% of the Indang object, 2.8% of a mono- rearrangement object, and 0.8% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 285g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.2% of a JI rearrangement object, and 0.5% of the Indang object.

Instead of 0.4 g of N.N-dimethylaniline used in example 6 Example 2, it reacted like Example 2 except having used 0.8 g of N.N-dimethylaniline. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 90.0% of a JI rearrangement object, 2.6% of the Indang object, 3.0% of a mono- rearrangement object, and 1.0% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 281g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.0% of a JI rearrangement object, and 0.3% of the Indang object.

Instead of 0.4 g of N.N-dimethylaniline used in example 7 Example 2, it reacted like Example 2 except having used 2.9 g of N.N-dimethylaniline. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 87.1% of a JI rearrangement object, 3.0% of the Indang object, 3.4% of a mono- rearrangement object, and 2.1% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 268g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.0% of a JI rearrangement object, and 0.3% of the Indang object.

[0012] Instead of the hydroquinone monomethyl ether 0.4 used in example 8 Example 2, it reacted like Example 2 except having used the hydroquinone monomethyl ether 0.08g. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.5% of a JI rearrangement object, 2.0% of the Indang object, 1.9% of a mono- rearrangement object, and 0.9% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 297g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 97.0% of a JI rearrangement object, and 0.4% of the Indang object.

Instead of the hydroquinone monomethyl ether 0.4g used in example 9 Example 2, it reacted

like Example 2 except having used the hydroquinone monomethyl ether 0.8g. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.4% of a JI rearrangement object, 2.0% of the Indang object, 1.8% of a mono- rearrangement object, and 1.0% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 297g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 97.0% of a JI rearrangement object, and 0.2% of the Indang object.

Instead of the hydroquinone monomethyl ether 0.4g used in example 10 Example 2, it reacted like Example 2 except having used the hydroquinone monomethyl ether 2.9g. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.2% of a JI rearrangement object, 2.2% of the Indang object, 1.6% of a mono- rearrangement object, and 1.2% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 293g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.9% of a JI rearrangement object, and 0.2% of the Indang object.

[0013] Instead of the N,N-dimethylaniline used in example 11 Example 2, it reacted like Example 2 except having used N,N-diethylaniline. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.6% of a JI rearrangement object, 2.0% of the Indang object, 1.8% of a mono- rearrangement object, and 0.5% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 301g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 97.2% of a JI rearrangement object, and 0.3% of the Indang object.

Instead of the N,N-dimethylaniline used in example 12 Example 2, it reacted like Example 2 except having used dimethylamino pyridine. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 90.1% of a JI rearrangement object, 2.1% of the Indang object, 1.6% of a mono- rearrangement object, and 0.6% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 281g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.2% of a JI rearrangement object, and 0.3% of the Indang object.

Instead of the N,N-dimethylaniline used in example 13 Example 2, it reacted like Example 2 except having used benzotriazol. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 87.6% of a JI rearrangement object, 2.8% of the Indang object, 1.3% of a mono- rearrangement object, and 1.2% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 264g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy

diphenylsulfone refined material were 96.0% of a JI rearrangement object, and 0.3% of the Indang object.

Instead of the N,N-dimethylaniline used in example 14 Example 2, it reacted like Example 2 except having used diethylenetriamine. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 88.7% of a JI rearrangement object, 2.8% of the Indang object, 1.2% of a mono- rearrangement object, and 1.0% of a monoallyl object. The 3,3'-diallyl-4,4'-dihydroxy diphenylsulfone refined material 264g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.0% of a JI rearrangement object, and 0.4% of the Indang object.

Instead of the N,N-dimethylaniline used in example 15 Example 2, it reacted like Example 2 except having used dimethylbenzylamine. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 87.9% of a JI rearrangement object, 2.7% of the Indang object, 1.3% of a mono- rearrangement object, and 1.2% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 260g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl-4,4'-dihydroxy diphenylsulfone refined material were 95.9% of a JI rearrangement object, and 0.5% of the Indang object.

[0014] Instead of the hydroquinone monomethyl ether used in example 16 Example 2, it reacted like Example 2 except having used 3,5-di-t-butyl-4-hydroxytoluene. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.0% of a JI rearrangement object, 2.1% of the Indang object, 1.9% of a mono- rearrangement object, and 1.0% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 297g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.6% of a JI rearrangement object, and 0.4% of the Indang object.

Instead of the hydroquinone monomethyl ether used in example 17 Example 2, it reacted like Example 2 except having used 2,2'-methylenebis (6-t-butyl-3-methyl phenol). The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.1% of a JI rearrangement object, 2.2% of the Indang object, 1.8% of a mono- rearrangement object, and 0.9% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 289g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.5% of a JI rearrangement object, and 0.4% of the Indang object.

Instead of the hydroquinone monomethyl ether used in example 18 Example 2, it reacted like Example 2 except having used 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 91.1%

of a JI rearrangement object, 2.2% of the Indang object, 1.8% of a mono- rearrangement object, and 1.0% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 289g was obtained by processing like Example 2. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 96.7% of a JI rearrangement object, and 0.4% of the Indang object.

[0015] Instead of 0.4g of dimethylaniline and the hydroquinone monomethyl ether 0.4g which were used in comparative example 1 Example 1, it reacted like Example 1 except having used 6.2g of N.N-dimethylaniline, and the hydroquinone monomethyl ether 6.2g. The HPLC composition ratios (area percentage) of the reaction mixture after a reaction were 83.5% of a JI rearrangement object, 8.3% of the Indang object, 6.5% of a mono- rearrangement object, and 2.1% of a monoallyl object. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 207g was obtained by processing like Example 1. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 92.0% of a JI rearrangement object, and 2.8% of the Indang object.

Except that the content alkali total amount used a 60 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone instead of the content alkali total amount used in comparative example 2 Example 1 being a 5 ppm (weight ratio) 4,4'-diaryl oxydi phenylsulfone, it reacted like Example 1. the HPLC composition ratio (area percentage) of the reaction mixture after a reaction -- 88.7% of a JI rearrangement object, 4.4% of the Indang object, 2.3% of a mono- rearrangement object, and 1.2% of monoallyl object *****. The 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material 256g was obtained by processing like Example 1. The HPLC composition ratios (area percentage) of the obtained 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone refined material were 93.0% of a JI rearrangement object, and 1.5% of the Indang object. The content alkali total amount of a 4,4'-diaryl oxydi phenylsulfone, the kind of amine compound and the amount used, and the kind and the amount of the antioxidant used that were used for Examples 1-18 are shown in the 1st table, and the composition ratio of a reaction mixture, the yield of a refined material, and the composition ratio of a refined material are shown in the 2nd table.

[0016]

[Table 1]

第1表-1

| | アルカリ総量 (ppm) | アミン化合物 | | 酸化防止剤 | |
|-------|-----------------|----------|--------------|-----------------|--------------|
| | | 種類 | 使用量 (重量%) | 種類 | 使用量 (重量%) |
| 実施例1 | 5 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例2 | 15 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例3 | 30 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例4 | 45 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例5 | 15 | ジメチルアニリン | 0.02 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例6 | 15 | ジメチルアニリン | 0.2 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例7 | 15 | ジメチルアニリン | 0.7 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例8 | 15 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.02 |
| 実施例9 | 15 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.2 |
| 実施例10 | 15 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.7 |

[0017]

[Table 2]

第1表-2

| | アルカリ総量 (ppm) | アミン化合物 | | 酸化防止剤 | |
|-------|-----------------|-------------|--------------|--|--------------|
| | | 種類 | 使用量 (重量%) | 種類 | 使用量 (重量%) |
| 実施例11 | 15 | ジエチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例12 | 15 | ジメチルアミノピリジン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例13 | 15 | ベンゾトリアゾール | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例14 | 15 | ジエチレントリアミン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例15 | 15 | ジメチルベンジルアミン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |
| 実施例16 | 15 | ジメチルアニリン | 0.1 | ジブチルヒドロキシトルエン | 0.1 |
| 実施例17 | 15 | ジメチルアニリン | 0.1 | 2,2'-メチレンビス-(6-tert-ブチル-3-メチルフェノール) | 0.1 |
| 実施例18 | 15 | ジメチルアニリン | 0.1 | 1,1,3-トリス(2-メチル-4-ヒドロキシ-5-tert-ブチルフェニル)ブタン | 0.1 |
| 比較例1 | 5 | ジメチルアニリン | 1.5 | ヒドロキノンモノメチルエーテル | 1.5 |
| 比較例2 | 60 | ジメチルアニリン | 0.1 | ヒドロキノンモノメチルエーテル | 0.1 |

[0018]

[Table 3]

第2表-1

| | 反応混合物組成 (%) | | | | 精製品収率 (%) | 精製品組成 (%) | |
|-------|-------------|-------|-------|--------|-----------|-----------|-------|
| | ジ転位体 | インダン体 | モノ転位体 | モノアリル体 | | ジ転位体 | インダン体 |
| 実施例1 | 92.3 | 1.7 | 1.8 | 0.8 | 74 | 97.1 | 0.2 |
| 実施例2 | 92.0 | 1.9 | 1.9 | 0.7 | 73 | 97.1 | 0.3 |
| 実施例3 | 91.3 | 2.3 | 1.6 | 0.7 | 70 | 96.5 | 0.3 |
| 実施例4 | 90.9 | 2.9 | 1.5 | 0.6 | 69 | 96.3 | 0.4 |
| 実施例5 | 90.5 | 2.0 | 2.8 | 0.8 | 69 | 96.2 | 0.5 |
| 実施例6 | 90.0 | 2.6 | 3.0 | 1.0 | 68 | 96.0 | 0.3 |
| 実施例7 | 87.1 | 3.0 | 3.4 | 2.1 | 65 | 96.0 | 0.3 |
| 実施例8 | 91.5 | 2.0 | 1.9 | 0.9 | 72 | 97.0 | 0.4 |
| 実施例9 | 91.4 | 2.0 | 1.8 | 1.0 | 72 | 97.0 | 0.2 |
| 実施例10 | 91.2 | 2.2 | 1.6 | 1.2 | 71 | 96.9 | 0.2 |

[0019]

[Table 4]

第2表-2

| | 反応混合物組成 (%) | | | | 精製品収率 (%) | 精製品組成 (%) | |
|-------|-------------|-------|-------|--------|-----------|-----------|-------|
| | ジ転位体 | インダン体 | モノ転位体 | モノアリル体 | | ジ転位体 | インダン体 |
| 実施例11 | 91.6 | 2.0 | 1.8 | 0.5 | 73 | 97.2 | 0.3 |
| 実施例12 | 90.1 | 2.1 | 1.6 | 0.6 | 68 | 96.2 | 0.3 |
| 実施例13 | 87.6 | 2.8 | 1.3 | 1.2 | 64 | 96.0 | 0.3 |
| 実施例14 | 88.7 | 2.8 | 1.2 | 1.0 | 64 | 96.0 | 0.4 |
| 実施例15 | 87.9 | 2.7 | 1.3 | 1.2 | 63 | 95.9 | 0.5 |
| 実施例16 | 91.0 | 2.1 | 1.9 | 1.0 | 72 | 96.6 | 0.4 |
| 実施例17 | 91.1 | 2.2 | 1.8 | 0.9 | 70 | 96.5 | 0.4 |
| 実施例18 | 91.1 | 2.2 | 1.8 | 1.0 | 70 | 96.7 | 0.4 |
| 比較例1 | 83.5 | 8.3 | 6.5 | 2.1 | 50 | 92.0 | 2.8 |
| 比較例2 | 88.7 | 4.4 | 2.3 | 1.2 | 62 | 93.0 | 1.5 |

[0020][Note] A presentation is HPLC composition ratio (area percentage).

JI rearrangement object: 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone. Indang object: 5-(3-allyl-4-hydroxy) phenyl sulfonyl 1-oxa 2-methylindan.

Mono- rearrangement object: 3-allyl-4-hydroxy-4'-allyloxy diphenylsulfone. Monoallyl object: 3-allyl-4,4'-dihydroxy diphenylsulfone.

As it sees in the 2nd table, the alkali total amount contained in a 4,4'-diaryl oxydi phenylsulfone is 5-45 ppm (weight ratio), In Examples 1-18 which performed the heating rearrangement reaction under the existence of 0.02 to 0.7 % of the weight of amine compounds, and 0.02 to 0.7 % of the weight of antioxidants, The yield of a refined material is high, there is much content of 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone, there is little content of a 5-(3-allyl-4-

hydroxy) phenyl sulfonyl 1-oxa 2-methylindan, and purity is high. It turns out that refined material yield and purity become high, so that there are few alkali total amounts, when the result of Examples 1-4 is seen. On the other hand, in both the comparative examples 1 that have too much amount of an amine compound and the antioxidant used, the yield of a refined material and purity are low. Also in the comparative example 2 with many alkali total amounts contained in a 4,4'-diaryl oxydi phenylsulfone, both the yield of a refined material and purity are low.

[0021]

[Effect of the Invention]According to this invention method, a ground fogging ingredient can manufacture little 3,3'-diallyl- 4,4'-dihydroxy diphenylsulfone with high purity with high yield.

[Translation done.]